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DETERMINATION OF THE DENSITY AND THE COMPRESSIBILITY OF ACETYLENE.

By Jitsusaburo SAMESHIMA.

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Material. The acetylene gas was prepared by the action of water on calcium carbide and then passed through tubes of copper sulphate solution, chromic acid solution, potassium hydroxide solution, solid calcium oxide and phosphorus pentoxide successively, and then frozen by liquid air.

Density of Acetylene. The density of the gas thus prepared was measured by the Dumas' method at 0°C. and 25°C. and under various pressures. The results are shown in the following table.

Temp. degree	Pressure atm.	Volume of the Dumas' bulb c.c.	Weight of acetylene gr.	Weight of one litre of acetylene gr.	Relative value of pv	
					Taking $pv=1$ at 25° and 1 atmosphere	Taking $pv=1$ at 0° and 1 atmosphere
0.00	0.5341	143.422	0.08951	0.6241		1.0053
„	0.6279	143.424	0.10539	0.7348		1.0038
„	0.9988	143.431	0.16837	1.1739		0.9995
„	1.0007	143.431	0.16852	1.1749		1.0005
„	1.5096	143.441	0.25597	1.7845		0.9938
„	1.0000	143.431	0.16849 *	1.1747*		1.0000
25.00	0.9972	143.534	0.15371	1.0709	1.0002	1.0939
„	1.0067	143.534	0.15522	1.0814	0.9998	1.0936
„	1.6391	143.546	0.25386	1.7685	0.9954	1.0888
„	1.0000	143.534	0.15416 *	1.0740*	1.0000	1.0937

* Obtained by interpolations.

The volume of the bulb was 143.4310 c.c. at 0° and 143.5338 c.c. at 25° when the pressure inside and outside were the same. The contraction of the bulb by the addition of one atmospheric pressure outside was determined by the method given in Travers' book[1], the result obtained being 0.0195 c.c. The third column of the table was calculated from these data.

The value of pv at 0°C. will be expressed by the linear equation $pv=1.0114-0.0114\,p$, for the pressure range between 0.5 and 1.5 atmospheres. If we calculate $(pv)_{p=0}$ from this equation we obtain $\frac{(pv)_{p=0}}{(pv)_{p=1}}=1.0114$.[2]

(1) Travers, Study of Gases, London, 1901, page 119.

(2) Howarth and Burt (*Chem. Abst.* 19 (1925) 3176) obtained the value $\frac{(pv)_1-(pv)_0}{(pv)_0}=-0.00884$ or $\frac{(pv)_0}{(pv)_1}=1.00892$.

The weights of one litre of acetylene under one atmosphere are given in the table, thus 1.1747 gr. at 0° and 1.0740 gr. at 25°. The mean expansion coefficient of the gas between 0° and 25° under one atmosphere is $\frac{v_{25}-v_0}{25\,v_0}=0.0037496$. The weight of one litre of acetylene at 0° and 1 atmosphere as determined by other authors is :

1.1712, Leduc, *Ann. Chim. Phys.*, **15**, (1898) 36.
1.1791, Stahrfoss, *J. Chim. Phys.*, **16**, (1918) 175.
1.1695, Maass and Russell, *J. Am. Chem. Soc.*, **40**, (1918) 1847.

Compressibility of Acetylene. Two calibrated tubes, one of which contained acetylene and the other hydrogen, were connected with each other and dipped in a thermostat. These two gases were subjected to compression simultaneously by means of a bomb of compressed air, and the change of volume of each gas was observed. The pressure was calculated from the change in the volume of hydrogen. The following values were used for the compressibility of hydrogen.

Pressure atm.	pv at 0°C.	pv at 25°C.
1	1.0000	1.0915
5	1.0024	1.0940
10	1.0055	1.0971
15	1.0086	1.1004

The results of observations and the values calculated therefrom are summarized in the following table.

Temp. degree	Volume of gases observed		Pressure atm.	Relative value of pv	
	Hydrogen c.c.	Acetylene c.c.		Taking $pv=1$ at 25° and 1 atmosphere	Taking $pv=1$ at 0° and 1 atmosphere
0.00	2.6484	1.6756	1.000		1.0000
„	1.6062	1.0076	1.650		0.9919
„	1.4890	0.9328	1.780		0.9907
„	1.0770	0.6703	2.461		0.9846
„	1.0321	0.6418	2.568		0.9837
„	0.5935	0.3624	4.472		0.9671
„	0.3677	0.2183	7.234		0.9425
„	0.2513	0.1446	10.600		0.9148
„	0.2467	0.1415	10.798		0.9119
„	0.2396	0.1353	11.263		0.9095
25.00	2.8930	1.8309	1.000	1.0000	1.0937
„	1.2027	0.7515	2.407	0.9881	1.0808
„	0.6604	0.4064	4.389	0.9742	1.0655
„	0.3982	0.2396	7.291	0.9541	1.0436
„	0.3341	0.1989	8.697	0.9448	1.0333
„	0.2560	0.1499	11.368	0.9307	1.0180

The following values of pv have been obtained by interpolations from the above tables.

Pressure atm.	pv at 0°C. (Taking $pv=1$ at 0° and 1 atm.)	pv at 25°C.
0.5	1.0057	1.0089
1.0	1.0000	1.0037
2.0	0.9891	1.0841
4.0	0.9708	1.0684
6.0	0.9530	1.0531
8.0	0.9360	1.0285
10.0	0.9194	1.0255
12.0	0.9026	1.0139

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THE RADIOACTIVE MANGANIFEROUS NODULES FROM TANOKAMI, OOMI PROVINCE.

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The feeble radioactive property of the characteristic black nodules from the bed of the Kichijo River, that runs along the Tanokami Hill, Oomi Province, has not been noticed until the author visited the locality in November, 1922. On that occasion, similar ones were also found embedded in a part of the rock body which lies just on the back of the hill side where the stream takes its rise. The nodules vary in size from about a half to two centimeters across, occurring as a pebbly constituent of the gravel-bed of the river, and are irregular in shape often with rounded edges. Some of them, often consisting, in the interior, of a mass of quartz pieces and grains of pale greenish clayey matter, are merely surrounded by a thin coating of the black material. Lying embedded in the rock which chiefly consists of coarse grains of quartz and the same clayey material as that which sometimes forms the inner parts of certain pebbly specimens, the nodules are considered to be composed of the essential black concretionary matter filling cracks of the rock.

Thin sections proved at once the black portion to be opaque and amorphous in structure, cementing abundant minute inclusions consisted of frag-

ments of quartz and other siliceous minerals, and its secondary nature was well brought out. The mean density, determined upon six pieces containing the inclusions which amounted to about sixty per cent of the material, was found to be 2.72. Both of the specimens were brittle with a hardness of about 3 and brown black to steel grey in colour. The luster was resinous, sometimes dull and coke-like, the fracture was often fibrous or concoidal and the streak brown or black. By treatment with hydrochloric acid, the black portion of the nodule was readily and completely dissolved with evolution of chlorine, leaving a considerable residue of nearly white sandy matters, and the solution mainly gave the reactions of manganese and iron.

Analysis. In selecting material for analysis it was found practically impossible to avoid siliceous inclusions. A number of specimens of both varieties, therefore, were separately pulverized, and the portions which contained least amount of inclusions were taken for analysis ; nevertheless, the insoluble gangue was present to the extent of 60 to 90 per cent as indicated in the analytical results mentioned below. Since the radioactive property was not detected in the insoluble portion, the investigation was principally directed to ascertain the composition of the soluble part. To carry out the analysis, the manganese was separated from iron and alumina by using barium carbonate in a neutral solution and by a basic acetate precipitation. The state of oxidation of manganese was determined by iodometry, that is to say, in measuring the quantity of iodine, which was liberated by the chlorine evolved by the action of hydrochloric acid upon the sample. The analytical results were as follows :

Constituents	Per cent in the pebbly nodule, found on the stream bed.		Per cent in the nodule, found on the hill side.
	(a)	(b) *	
Residue insoluble in hydrochloric acid	68.57	69.26	89.66
MnO_2	14.64	15.76	4.55
MnO	3.69	(as Mn_3O_4)	(as Mn_3O_4)
Fe_2O_3	4.66	4.70	1.20
Al_2O_3	0.78	0.83	0.82
PbO	—	—	0.40
CuO	—	—	trace
ZnO	—	—	0.31
CaO	0.74	(not looked for)	—
Ignition loss, less oxygen due to conversion of MnO_2 to Mn_3O_4	6.75	(not looked for)	2.95
Oxygen due to $MnO_2 \longrightarrow Mn_3O_4$	—	—	0.40 **
	99.83		100.29

* Determined on a separately powdered portion of the same sample.

** Assuming that the ratio of MnO_2 to MnO is the same as the pebbly nodules.

In the insoluble residue of the pebbly nodule mentioned in the above table contains 55.9 per cent of silica, while 70.0 per cent of silica was found in the nodule from the hill side. The following table contains the results of the analysis recalculated excluding the insoluble part. For the purpose of comparison, some of analysis of wads given in Dana's Mineralogy[1] were quoted in the same table, together with the author's results.

Constituents	The pebbly sample	The hill-side sample	Wad	
			(A)	(B)
MnO_2	49.7	59.8	66.2	68.9
MnO	12.6		7.9	7.5
Fe_2O_3	15.8	14.6	—	2.2
Al_2O_3	2.6	9.9	—	
PbO	—	4.8	0.2	—
CuO	—	(small)		—
ZnO	—	3.7	1.6	—
CaO	2.5	—	5.0	14.4(BaO)
H_2O	16.8	7.2	15.3	5.1
(MgO & Na_2O)	—	—	3.8	—
Total	100.0	100.0	100.0	98.1

The water was calculated from the ignition loss taking in consideration of the necessary correction for the oxidation of the manganese and the evolution of oxygen. Since the material of the rock body in which the nodules were included is practically identical with the insoluble residue previously described, similar determinations on the ignition loss were made on some pieces of the mother rock. The difference of these two determinations furnishes an approximate value of the water for the soluble part of the nodules, taking the percentage of the insoluble portion into consideration.

On the examination of the arc spectra taken by means of a quartz spectrograph, it was shown that besides the lines of the elements above described those of lead, copper, cobalt and molybdenum were detected in the soluble portion of the pebbly sample. The residue from the insoluble portion which was obtained by expelling silica by repeated evaporations with hydrofluoric acid and sulphuric acid, gave the lines of copper, tin, iron, aluminium, zinc and manganese. And in the zinc fraction of the hill-side sample, the lines of aluminium and cobalt were observed.

On the whole, it may be said that the chemical compositions of these two kinds of nodules are nearly the same and they belong to the same mineral. The analytical results, as well as the physical properties of the

(1) E. S. Dana, System of Mineralogy, IV Edition, p. 258.

soluble portion pretty resemble with those of certain wads, except the facts that the former contains some iron oxide.

The Radium Content. Though none of radioactive constituents was chemically detected in both of the nodules, they clearly show a feeble radioactivity, when roughly examined by means of an alpha-ray electroscope. The following results, compared with the activity of uranium oxide, were obtained.

Materials examined.	Activity per gr.
Uranium oxide (as a arbitrary standard)	100.
Hokutolite from Shibukuro (for the comparison)	3.5
The pebbly sample (siliceous inclusions: 70.4%)	1.3
The hill-side sample (siliceous inclusions: 92.0%)	2.0
The insoluble residue, obtained from the pebbly sample by once extraction with HCl	0.25
Pieces of the rock, in which the nodules were found embedded	0.1
A mass of minute biotite flakes, collected on the bed of the Kichijo River	0.00
Pieces of a rock, stained black with the manganese oxide, collected on the river bed	0.2

Thus it appears that the radioactivity is almost concentrated in the soluble portion of the nodules, namely, in the black manganiferous matter. The activity is, however, so feeble that it needs exposures of more than three weeks in order to give the distinct effect on a photographic plate. Accordingly, there was no proper means for determining the radioactive constituents in these specimens except the measurement of the radium content. The estimation method of radium simply consisted in boiling about one gram of the powdered sample with about 4 c.c. of concentrated sulphuric acid in a test tube made of quartz glass. The emanation liberated was transferred into an emanation electroscope of the Soddy's type[1], and its effect on the rate of leak was measured in the usual way. The electroscope was standardized by using an aliquot portion of a preparation of barium-radium chloride which was previously evaluated by the γ-ray method. The constant of the electroscope, thus determined, was 24.8×10^{-12} (*i.e.* one division per minute = 24.8×10^{-12} gr. radium). The results obtained are given below, the activities recorded being the means of several observations.

(1) F. Soddy, *Phil. Mag.*, [6], 18 (1909) 846.

Substances	Sample taken (gr.)	Activity (div. per min.)	Amount of Ra. (%)
The pebbly nodule	0.9139	4.24	1.15×10^{-8}
The hill-side nodule	1.3273	6.95	1.30×10^{-8}
" " "	0.9929	5.27	1.32×10^{-8}

As the whole activity is, however, attributed to the soluble part of the nodules, it follows that the amount of radium in the soluble portion of the pebbly nodule is 3.88×10^{-8} per cent, and that of the hill-side nodule 1.64×10^{-7} per cent. Thus the most remarkable character of these nodules is the fact that they contain radium in the black soluble portion, the amount of which is nearly thousand times that of the ordinary igneous rocks. The ordinary igneous rocks contain generally about 10^{-10} per cent of radium. And as might be expected, the nodules found on the river bed carries somewhat less amount of radium which is considered to have been lost probably under the action of stream water. Besides these nodules there are found in the same river bed, several rock blocks, impregnated with this radioactive secondary manganese iron oxide. This fact suggests the previous existence of primary uranium bearing minerals in this vicinity.

In conclusion, the author wishes to thank Messrs. J. Sasaki and J. Ooe for their laborious assistance in collecting the minerals, and Mr. J. Yoshimura for help in the spectroscopic examination.

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ON THE ANOMALOUS DISPERSION AND ABSORPTION OF ELECTRIC WAVES. I.[1]

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We know that the dielectric constants of many liquid substances have such values that their square roots (*i.e.* the refractive indices for the long electric waves) are incomparably greater than the indices of refraction for the visible and infra-red rays. These substances are, in general, chemically abnormal liquids. So if the refractive indices (n) for the electromagnetic waves of the wave lengths ranging from the order of those of visible light to

(1) Read before the Chemical Society of Japan, January 17, 1925.

infinity be measured, we may expect that n suffers an enormous change or changes in a certain region of wave length till it attains the large value which is practically independent of wave length. Such a change (*i.e.* an anomalous dispersion) will be accompanied by an anomalous absorption, if the phenomenon be regarded as analogous to that in the case of the shorter wave lengths.

Although some authors measured the indices[1] of refraction and absorptions[2] of short electric waves, the measurements were carried out only at the ordinary temperatures and at the wave length of less than one meter. The following experiments have been undertaken to measure the anomalous dispersion and absorption at various temperatures and for various wave lengths, and to study their relations. In this first report, however, only the description of the experiment by use of the wave of 6.1 meters will be given.

The resonance method is adopted in this experiment. As a oscillation generator, a thermionic bulb is used. Fig. 1 shows the scheme of the generator circuit. H is a high-tension battery of 200 volts, F a filament battery of 6 volts, I_F an ammeter which indicates the filament current aud I_A a milliammeter in the anode circuit. H is connected in parallel with the air condenser, the capacity of which is about 1/1000 M.F. A resistance of 10000 ohms shunted by a condenser (also 1/1000 M.F.) is inserted in the grid circuit.

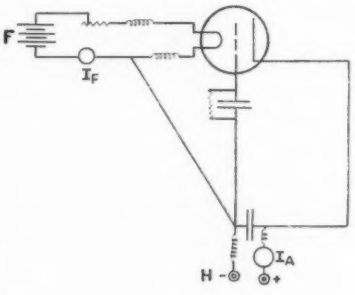

Fig. 1

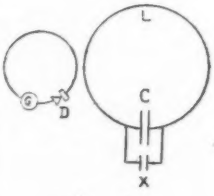

Fig. 2

The resonator consists essentially of an inductance L and the two capacities C and X as shown in Fig. 2. C is constructed from two brass bars of rectangular section (9 mm. $\times$ 5.5 mm.) placed in parallel position at a distance of 5.5 mm. Between these two, a plane-parallel glass plate is slided to vary the capacity of C. The liquid to be examined is contained in a small vessel X of about 20 c.c. with platinum wires fused in on opposite sides. The vessel X is con-

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(1) Lampa, *Wien. Ber.*, **105** (1896) 587 u. 1049.
Lang, *Wien. Ber.*, **105** (1896) 253.
Möbius, *Ann. d. Phys.*, **62** (1920) 293.
Tear, *Phys. Rev.*, **II. 21** (1923) 611.

(2) Drude, *Z. physik. Chem.*, **23** (1897) 308.
Romanoff, *Ann. d. Phys.*, **69** (1922) 125.

nected in parallel with C. The detector circuit consists of a crystal detector D and a sensitive galvanometer G. All the resonating system is placed so far from the oscillator that the change of the resonating current (or the current at resonance) causes no effect upon the wave length of the oscillator.

At first the second system is adjusted to resonance to the first by sliding the glass plate of C into its suitable position, then the capacity X is filled with the liquid to be examined and the system is again brought into resonance by the same method. If the sample has no absorbing power, the resonating currents will be the same in both cases. This has been shown to be actually the case for normal organic liquids. But if the sample absorbs electric wave, for instance glycerine, the resonating current in the latter case is always considerably less than that in the former.

When the waves of a few meters were used, distilled water, acetone, benzene, the mixtures of acetone and water and those of acetone and benzene show no change of resonating current at ordinary temperatures. This is also the case when the capacity of X is changed to a considerable amount. From these results it is evident that these are non-absorbents of this wave and can be used as standard substances in the measurement of dielectric constants. In order to determine specific constants of each vessel measurements were carried out by use of these non-absorbing substances and the results show that the relation expressed by the equation (1) holds within the limit of experimental error which amounted to a few percent. The effect of reading wires from C to X which have certain small inductance are not perceptible.

$$\varepsilon - 1 = k \Delta C \quad \cdots\cdots(1)$$

ε is the dielectric constant ofthe liquid, k the specific proportional constant for the vessel, and ΔC the displacement of the glass plate from the initial position *i.e.* the position when X is filled with air only.

Merck's or Kahlbaum's reagents were used in the experiments. They were dehydrated and then subjected to fractional distillations before use.

Wave Length. If the resonating circuit is placed so far from the detector circuit that the mutual inductance is negligible, the wave length of the oscillation circuit can be calculated from the self inductance and capacity of the resonator. For this self-inductance a simple circle of copper wire were used in order that the self-inductance L can be calculated from the following formula (L–inductance, R–radious of the circle, ρ–radius of the wire used),

$$L = 4\pi R(\ln R/\rho + 0.079) \cdots\cdots(2)$$

The variable capacity was calibrated, using disc condensers as the standard, the capacities of which were obtained from the following formula:

$$K = \frac{r^2}{4a} + \frac{r}{4\pi}\left(\ln \frac{16\pi r(a+d)}{a^2} + 1 + \frac{d}{a} \ln \frac{a+d}{d}\right) \cdots\cdots(3)$$

where K is the capacity, r the radius of the disc, d its thickness, and a the distance between two discs. Table 1 contains the observed values of wave length using various combinations of inductance and capacity. The wave length is 6.1 meters.

TABLE 1.

Inductance cm. (E.M.U.)	Capacity cm. (E.S.U.)	Wave Length m.
413	22.7	6.08
490	19.0	6.06
603	15.45	6.07
622	15.0	6.07

Mean 6.1 Meters

Dielectric Constants and Absorptions. The values of the dielectric constants and the absorptions (expressed by the change of the resonating current) at various temperatures are shown in Table 2. When the substance under examination is an absorbent, X is not a pure capacity but corresponds to a capacity shunted by a considerably low resistance. As the values of ε of such a substance were also calculated from the equivalent pure capacity, the values are only apparent in such a case. Several vessels were used to avoid the constant error characteristic to each vessel. The capacities of Vessels I. II. III are in the ratio 1 : 1.2 : 1.5.

TABLE 2.

ΔC: Displacement of the glass plate. ε: Dielectric constant. I and I_0: Resonating current when X is filled by the sample and by the air respectively.

Acetone.

Temp.	Vessel II.		
	ΔC	ε	$\frac{I}{I_0}$
41	3.0	18	1.0
24	3.3	20	1.0
12	3.3	20	1.0
− 3	3.5	21	1.0
−13	3.92	23	1.0
−22	4.1	25	1.0
−36	4.3	26	1.0
−49	4.7	28	1.0
−68	6.0	30	1.0
−69	6.4	32	1.0

Glycerine.

Temp.	Vessel I.			Vessel III.		
	ΔC	ε	$\frac{I}{I_0}$	ΔC	ε	$\frac{I}{I_0}$
57	4.8	36	.4	8.2	35	.2
46	5.0	37	.3	8.7	37	.2
37	5.2	39	.2	9.3	40	.08
30	5.3	40	—	9.6	41	—
24	5.4	41	.08	9.7	42	.04
20	5.2	39	.05	9.4	41	.03
18	5.1	38	—	9.2	40	—
15	5.0	38	.04	8.7	37	—
6	3.25	25	.05	5.4	24	—
− 8	1.45	12	.08	2.2	10	—
−23	0.8	7	.5	1.1	6	.2
−45	0.4	4	.9	0.7	4	—
−70	0.35	4	1.0	0.6	4	1.0

Methyl alcohol.

Temp.	Vessel I		Vessel III	
	ε	$\frac{I}{I_0}$	ε	$\frac{I}{I_0}$
45	28	.6	27	.4
33	29	.5	29	.4
18	32	.5	33	.2
14	—	—	—	—
10	35	.3	34	.2
0	37	.3	37	.2
− 4	—	—	—	—
− 9	39	—	39	.2
−28	44	.2	—	—
−42	49	.1	—	—
−44	—	—	—	—
−54	54	.09	—	—
−65	55	.08	—	—
−69	57	.04	—	—
−77	58	—	—	—
−84	62	.04	—	—
−89	—	—	—	—

Ethyl alcohol.

Temp.	Vessel I		Vessel III	
	ε	$\frac{I}{I_0}$	ε	$\frac{I}{I_0}$
63	18	.9	18	.8
53	19	.8	19	.7
45	21	—	20	—
34	22	.6	22	.5
25	24	—	23	.4
20	24	.6	23	.3
10	26	.5	25	.3
8	27	.4	26	—
− 4	28	.3	27	.2
−13	30	.2	29	.1
−18	30	.2	29	.1
−23	31	.1	—	—
−30	32	.1	31	.04
−32	31	.07	—	—
−35	—	—	32	.05
−46	31	—	30	—
−48	29	.05	29	.03
−58	22	.06	25	.03
−60	—	—	23	.03
−69	19	.05	18	.03
−71	19	.05	—	—

Propyl alcohol.

Temp.	Vessel I		Vessel III	
	ε	$\frac{I}{I_0}$	ε	$\frac{I}{I_0}$
60	15	.9	15	.8
50	16	.9	16	.7
45	17	.8	16	.6
36	18	.7	17	.6
26	19	.6	19	.4
23	20	.5	19	.3
16	22	—	20	.3
15	22	.4	20	—
6	—	—	21	.2
3	23	.2	21	.1
− 8	23	.2	22	.1
−20	21	.1	21	.05
−31	17	.05	17	.03
−41	13	.07	11	.05
−51	8	.1	8	.06
−59	6	.2	6	.1
−69	5	.2	5	.1

Isopropyl alcohol.

Temp.	Vessel I		Vessel III	
	ε	$\frac{I}{I_0}$	ε	$\frac{I}{I_0}$
55	15	.9	14	.8
45	16	.9	15	.7
37	16	.8	16	—
29	17	.7	—	—
26	19	.6	18	.4
20	19	.5	—	—
16	20	.5	20	.3
9	21	.3	—	—
3	21	.3	21	.2
− 4	21	.1	—	—
− 8	23	.1	22	.05
−16	22	.08	22	.03
−19	19	.04	—	—
−29	16	.08	17	—
−31	13	.09	—	—
−39	10	.1	—	—
−42	8	.1	9	.05
−47	7	.2	—	—
−54	5	.2	6	.1
−56	6	.2	—	—
−69	4	.4	5	.2

Butyl alcohol.

Temp.	Vessel I		Vessel III	
	ε	$\frac{I}{I_0}$	ε	$\frac{I}{I_0}$
59	13	.8	—	—
58	—	—	13	.7
48	14	.6	14	.5
37	16	.5	15	—
27	17	.4	16	.2
18	17	.2	18	.1
16	18	—	18	.1
13	18	—	18	—
8	19	—	19	—
7	19	—	19	.07
4	19	—	—	—
− 4	18	.06	18	.03
− 9	18	—	18	—
−15	17	.09	18	.03
−22	—	—	12	—
−29	10	.1	11	.05
−37	7	—	7	—
−47	6	.2	5	.1
−67	4	.4	4	.2

Isobutyl alcohol.

Temp.	Vessel I		Vessel III	
	ε	$\frac{I}{I_0}$	ε	$\frac{I}{I_0}$
57	13	.8	12	.8
45	14	.8	13	.6
38	15	.7	15	.6
30	16	.5	15	.3
22	16	.4	16	.2
18	17	.3	17	.1
16	18	.2	17	.1
10	18	.2	18	.09
1	18	.2	17	.09
−10	13	.1	13	.04
−19	9	.09	9	.07
−28	6	—	6	.08
−42	5	—	5	.2
−53	4	.5	4	.2
−58	4	.6	3	.4
−62	—	—	3	.6
−63	4	.7	—	—

Amyl alcohol.

Temp.	Vessel I		Vessel II		Vessel III	
	ε	$\frac{I}{I_0}$	ε	$\frac{I}{I_0}$	ε	$\frac{I}{I_0}$
63	10.4	—	—	—	10	.7
56	—	—	11	.8	—	—
50	12	—	—	—	11	—
45	—	—	12	.6	—	—
39	13	.7	—	—	12	.5
35	—	—	13	.5	—	—
31	14	.4	—	—	14	.3
29	—	—	13	.4	—	—
24	15	.4	—	—	14	.2
20	—	—	14	.3	—	—
16	15	.2	14	.2	14	.2

Temp.	Vessel I		Vessel II		Vessel III	
	ε	$\frac{I}{I_0}$	ε	$\frac{I}{I_0}$	ε	$\frac{I}{I_0}$
14	15	.2	—	—	15	.1
9	—	—	14	.09	—	—
4	13	.1	—	—	14	.08
− 4	—	—	12	.06	—	—
−10	9	.1	—	—	9	.06
−11	—	—	9	.06	—	—
−20	7	.2	7	—	6	.08
−33	4	.3	5	.3	4	.2
−41	4	.5	3	.4	4	.3
−48	4	.5	3	.5	4	.4
−55	—	—	3	.6	—	—

Acetone. The resonating currents show no change at all temperatures. The value of ε increases as the temperature is lowered. Nothing anomalous can be found.

Glycerine. The behavior is quite different from that of acetone. Though ε changes at higher temperatures quite similarly to that of an ordinary substance, it attains a maximum value near ordinary temperature, then it decreases till it attains a value almost equal to the square of the refractive indices for visible light. As to the resonating current it decreases as the temperature is lowered, then it passes through a minimum and at last I/I_0 becomes unity. The small value of ε at the low temperature is no more an apparent one, because there is no absorption at all. Thus in this case the change of dielectric constants is quite different from that of an ordinary substance, though we are not still aware of its true value for the case in which the absorption takes place. It is evident that we are dealing here with an anomalous dispersion accompanied by an anomalous absorption as was expected.

Alcohols. Of alcohols—ethyl, propyl, isopropyl, butyl, isobutyl and amyl, the results are, in general, similar to that of glycerine. Methyl alcohol gives no maximum of apparent dielectric constants, but as there exists a considerable anomalous absorption at lower temperatures it can be expected that at still lower temperatures it will also show an anomalous change of ε.

As given above, these alcohols, monovalent as well as polyvalent, show anomalous absorptions accompanied by anomalous dispersions of the electromagnetic oscillation of the wave length of 6.1 meters. It seems that the cause of this absorption lies in the hydroxyl group contained in these compounds(1). This fact, therefore, may be used as one of the criterions to ascertain whether a compound contains this group or not. From the point of view of the classical electro-magnetic theory these substances must have their characteristic oscillations, the wave length of which corresponds to that used in this experiment. Then it should be admitted that the wave length of these characteristic oscillations varies with the temperature.

In conclusion I desire to express my best thanks to Prof. M. Katayama for his kind guidance and to Assistant Prof. D. Nukiyama for his advice on electricity.

October, 1924.

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(1) Drude, *loc. cit.*

CATALYTIC ACTION OF REDUCED COPPER ON OXIMES. (ON BECKMANN'S REARRANGEMENT. XVI.)

By Shozo YAMAGUCHI.

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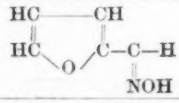
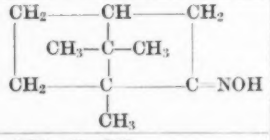
Since the first report of these researches was published by the writer and Professor Komatsu[1], the present writer has described some experimental results on the same subject, which are now summarised with the present experiment in the following table:

Oxime used	Reaction product in mol %				
	$RCONH_2$	RCN	RCOOH	Base	$\frac{R}{R'}>C=O$
1. $C_6H_5-C(=NOH)-H$	51.9	27.5	20.6	–	–
2. 	44.6	–	trace	trace	55.4
3. $C_6H_5CH=CH-C(=NOH)-H$	–	+	–	trace	+
4. $C_6H_5-C(=NOH)-NH_2$	58.3	29.3	12.4	–	–
5. $C_6H_5CH_2-C(=NOH)-CH_2C_6H_5$	11.2	12.9	11.2	–	64.7
6. 	+	+	+	trace	+
7. $C_6H_5-C(=NOH)-CH_3$	–	+	+	+	+
8. $CH_3-C(=NOH)-CH_3$	–	–	–	+	+
9. $C_6H_5-C(=NOH)-C_6H_5$	–	–	–	trace	+
	Diphenyl-ketimine 3.3	Tetraphenyl-ethane 17.8	Diphenyl-methane 46.1		Ketone 32.8

(1) *The Memoirs Coll. Sci. Kyoto Imp. Univ.*, **6**, (1923) 245; **A, 7**, (1925) 281; **A, 9**, (1925) 35.

When the oximes of different ketones or aldehydes are passed on reduced copper heated at about 200° in an atmosphere of hydrogen, as will be seen in the above table, yield acid amide ($RCONH_2$), nitrile (RCN), acid (RCOOH), bases ($R_2C{=}NH$, R_2CHNH_2, $(R_2CH_2)_2NH$, NH_3) ketone or aldehyde and hydrocarbons (R_2CH_2) and ($R_2CH)_2$. The yields of these compounds seem to depend more or less on the structure of the oximes; by hydrolysis all oximes excepting benzaldoximes and benzhydroxamic acid yield principally the ketones or aldehydes from which the oximes were derived, the oximes of cinnamyl aldehyde, of acetone, of acetophenone and of benzophenone yield an acidamide of the type $RCONH_2$ as the main reaction product.

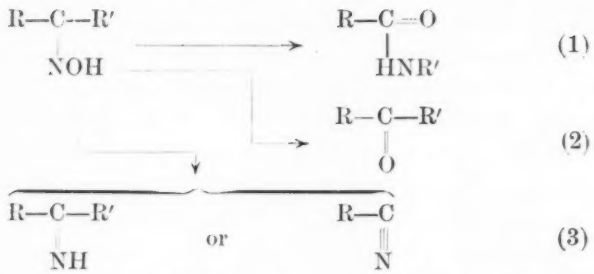
The oximes, thus, will be classified into three groups according to the chemical nature of the principal reaction products by the contact action of reduced copper at 200°.

1st. Group. The oxime of this group yields aldehyde or ketone and some basic compounds as the main reaction products, and the benzophenone and acetone oximes belong to this group. The carbonyl compound resulting by the hydrolysis of the oxime, will be transformed into hydrocarbons by the further catalytic action of reduced copper in an atmosphere of hydrogen, as actually observed in the case of benzophenone oxime.

2nd. Group. Benzaldoxime and benzhydroxamic acid each yields an acid amide which by the contact action of reduced copper, is transformed into nitrile and acid.

3rd. Group. The oxime of this group stands between the two groups of oximes above-mentioned in its behavior toward reduced copper heated at 200°, and yields the acid amide and carbonyl compounds with some basic ones. Their relative amount in the reaction product depending more or less upon the chemical or electronical nature of the hydrocarbon radicals linked to the carbon atom of the methane nucleus of the oxime. Furfuraldoxime, cinnamylaldoxime, dibenzylketoxime, camphoroxime and acetophenone oxime belong to this group.

As a matter of fact, aldoximes and ketoximes or their salts, probably suffer the chemical reactions from heat, being transformed directly; (1) into its isomeric acid amides—Beckmann's rearrangement; (2) into carbonyl compounds—aldehyde or ketone by hydrolysis; (3) into imine or nitrile by dehydration and the latter substance will also result from an acid amide:



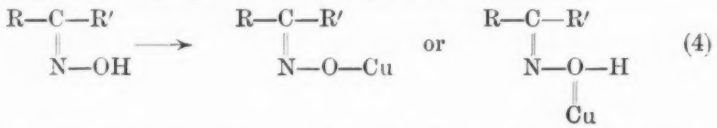
(1)

(2)

(3)

Such direct transformations of the oximes or their salts by heat would take place independently or simultaneously according to the chemical nature of the oximes. In presence of reduced copper, the velocity of these reactions will also evidently be modified, some reactions being accelerated and others retarded, and as a consequence, the oxime, from the view point of the nature of chemical reactions, were classified into the three groups mentioned above.

With regard to the catalytic action of reduced copper on the behavior of the oxime toward heat, the writer has attempted to explain its mechanism with the following interpretations. When an oxime is passed in a vapour state over finely divided copper, it would be condensed in a thin layer on the surface of the catalyst, and temporarily form a compound—a salt or an oxonium compound,—though its combination is in a labile state.

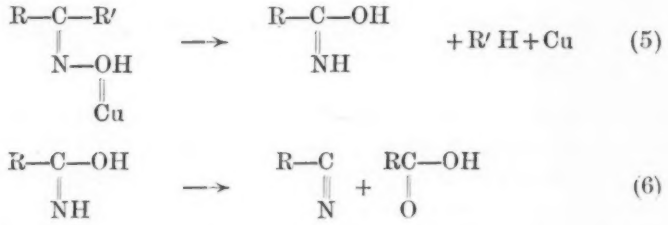


(4)

Moreover, in the present case, an hypothetical substance of the composition CuH_2 should occur in the reaction system, since hydrogen is spread uniformly in the reaction system. The dissociation of these compounds will take place, in the course of evaporation, on the surface of the metal, and where the chemical transformations mentioned above take place. During the evaporation of the oxonium compound on the surface of the catalyst, the combining force between the hydrocarbon radicals and the carbon atom of the methane nucleus of the oxime is smaller than that between the nitrogen and the carbon atoms. Moreover, when the metal combined with the oxime behaves to lose the strength of the former affinity by acting as a donor of electrons, as sodium does in the molecular rearrangement of the oxime observed by S. Komatsu and T. Hiraidzumi[1]. The molecular rearrangement of the oxime into its isomeric acid amide will take place with a prominent yield, but in the meantime, the hydrocarbon radical detached by the influence of

(1) *The Memoirs Coll. Sci. Kyoto Imp. Univ.*, A, 8, (1925) 273.

the catalyst, is left in a free state without entering into combination with the nitrogen atom, and as a consequence the simple acid amide of the formula $RCONH_2$ results, and this by the further action of the catalyst is soon transformed partly into nitrile and acid, which may be represented by the following scheme:



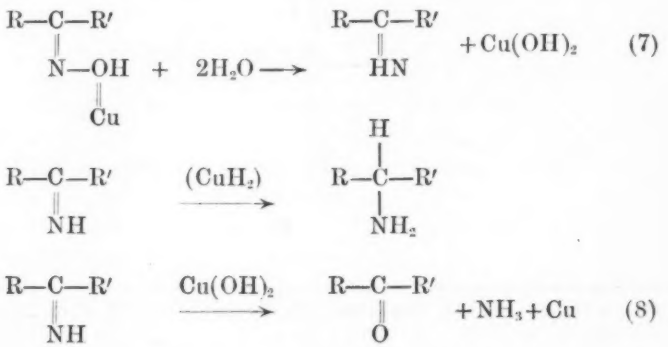
(5)

(6)

The transformation of the second group of oximes into acid amide, nitrile and acid by the contact action of the catalyst, will be represented by the schemes (1) and (6).

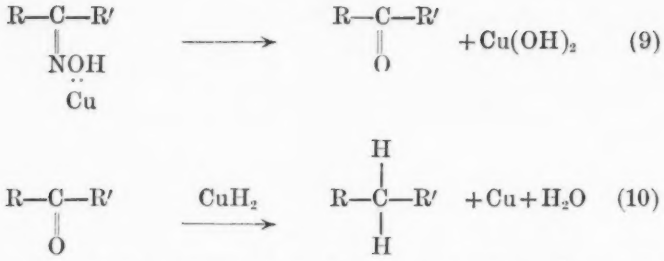
When however, the linkings between the hydrocarbon radicals or the hydrogen and the carbon atom of the methane nucleus of the oxime are quite strong, and the metal exerts no appreciable influence on these affinities, the hydrolysis will results in the formation of an aldehyde or a ketone, one part of which will be reduced into hydrocarbon, by the catalytic action of reduced copper in an atmosphere of hydrogen as noticed in the case of the benzophenone oxime. The hypothesis would be applied to the explanation of the reactions of the first group of oximes.

If the dissociation of the linking between the hydroxyl group and the nitrogen atom, by heat or by the catalytic influence of reduced copper, takes place very easily, then the formation of imine or nitrile will occur and the conversion of the imine into base or ketone by catalytic reduction or hydrolysis in presence of the catalyst will take place in turn:



(7)

(8)



(9)

(10)

The behavior of the oximes of the first group, by the contact action of reduced copper will be represented in schemes (7) (8) and (10).

As was mentioned in the previous article,[1] the chemical reactions of the oximes will depend more or less upon the chemical and electronical nature of the hydrocarbon radicals, or in other words, the mobility of the radicals from the carbon atom of the methane nucleus depending mostly upon their electronical character, and also upon the catalytic influence of the catalyst presented in the reaction system, and all of the reactions shown in the schemes (1) (7) (8) and (10) would take place of some oximes belonging to the 3rd. group, possessing the chemical characters of both groups, in some degree. The conception of these ideas with respect to the conversion of the oxime into the acid amide, the carbonyl compound, and bases was thus fully illustrated by the experimental results mentioned in the above table.

January 1925.

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(1) S. Komatsu and T. Hiraidzumi, *The Memoirs Coll. Sci. Kyoto Imp. Univ.*, A, 8, (1925) 273.